

Assessment and Modeling of Adsorption Capacity of a Cationic Dye on the Natural Silica of El-Aouanajjel in North-Eastern Algeria.

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Abstract: The aim of this work is to study the adsorption of basic dye, methylene blue (MB), from an aqueous solution onto natural silica. The adsorption of MB by natural silica was carried out in static mode. Effects of parameters such as mass of adsorbant, initial dye concentration, stirring velocity, temperature, and pH on adsorption were investigated. In order to study the mechanism of the adsorption process, three kinetic models including pseudo-first order, pseudo-second order, and intra-particle diffusion were used. In addition, the linear Langmuir and Freundlich models were applied to describe equilibrium isotherms. The experimental results of adsorbent/adsorbate equilibrium show that the adsorption was well described by the kinetic model of pseudo-second order and by the Langmuir adsorption isotherm model. Optimal conditions for the adsorption of MB by natural silica were found to be: $V_a = 200$ rpm, $T = 25^\circ\text{C}$, and $\text{pH} = 8$.

Keywords: Adsorption; Dye, Silica, Isotherm, Kinetic model.

1 Introduction

Textile industry consumes very great quantities of water. Their rejects cause deteriorations of the aquatic environment because of their loads in stable dyes, very toxic and slightly biodegradable. Many studies^{1,5)} showed toxic effects of dyes, which require their treatment before being rejected in natural environment. Many techniques such as coagulation/flocculation^{6,8)}, chemical oxidation^{9,11)}, membrane filtration^{12,14)}, biodeterioration^{15,18)}, have been used for the treatment of waters containing dyes. However, much of these technologies are expensive, especially when they are applied for high flow effluents. Consequently, adsorption seems to be well adapted to textile industry¹⁹⁾ because of its proven effectiveness in elimination of organic pollutants and also for economic considerations^{20,21)}. The activated carbon is one of the most used adsorbents for the reduction of dyes, but it remains very expensive²²⁾. Hence, researches were then directed towards treatment processes using available, effective and low cost adsorbents, such as clays^{23,25)} and agricultural waste^{26,30)}.

The present study relates to the discoloration of our MB aqueous solution by the adsorption of this latter on natural silica available into large quantities at El-Aouana-Jijel (north east of Algeria) and may contribute to the development of a technically reliable and economically viable technology for the treatment of water contaminated by textile dyes.

2. Materials and Methods

2.1. Materials

- **Adsorbent**

The material used in this study is the natural silica of El-Aouana-Jijel (Algeria). The size particle distribution was measured by a laser granulometer-MalverneMastersizer. Only the particles of size lower than 100 μ m were used.

2.2 Characterization of ESM natural silica

The chemical composition was determined using a X-ray fluorescence (ARL Thermo Scientific Perform X), the morphology of natural silica was characterized using scanning electron microscopy (SEM) (Philips XL30) Surface functional groups of ESM were checked by Fourier transform infrared analysis (FTIR) using IR-1 affinity in combination with a single attenuated total reflectance reflection. The crystal structure of ESM was characterized on X-ray diffraction (XRD) (Model PW1710 Philips) using copper radiation $K\alpha$ ($\lambda = 1.5460 \text{ \AA}$), a generator setting of 40 kV, 40 mA, scanning speed 0.01 min⁻¹ and an angle of 2θ between 0 and 70...

- **Adsorbate**

The dye used in this study is the methylene blue (chloride 3,7-bis (dimethylamino) phenazathionium) obtained from Sigma-Aldrich with the chemical structure represented on Fig.1.

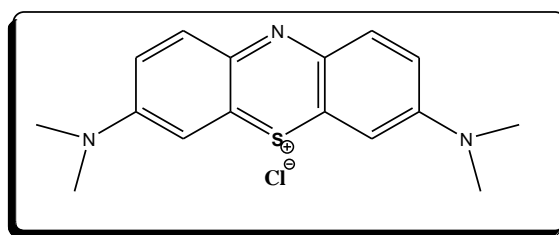


Fig 1: Chemical structure of methylene blue

2.3 Methods

2.3.1 Effect of the mass of adsorbent

With an aim of determining the necessary quantity of silica corresponding to an optimal elimination, a series of suspensions containing 20 ml of an aqueous solution containing 80 ppm of MB and a mass of silica varying from 0.05g to 0.5g has been prepared in pyrex tubes.

2.3.2 Elimination kinetics

Adsorption kinetics of MB for the various operating conditions (initial concentration, stirring velocity,

and temperature) were carried out in static mode. 22.5g/L of silica (result determined in the study of the effect of the mass of material) were mixed with a solution of MB.

The suspensions were stirred using a mechanical agitator. Over time, a volume of supernatant is prelevated and after centrifugation the concentration of MB is determined using a UV-VIS spectrophotometer (TECHCOMP 8500) at $\lambda_{max} = 665nm$. The pH of the suspensions varied between 6.8 and 7.1 without any adjustment.

The effectiveness of elimination of MB is calculated by equation (1):

$$R = \frac{C_0 - C_e}{C_0} \quad (1)$$

Where, R is the yield (%); C_0 and C_e are, respectively, the initial and equilibrium concentrations ($mg.L^{-1}$)

The quantity of adsorbed MB, q_e , was calculated using equation (2).

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (2)$$

Where $q_e (mg.g^{-1})$ is the capacity of adsorption at equilibrium; C_0 and C_e are, respectively, the initial and equilibrium concentrations

($mg.L^{-1}$); V(L) is the volume of the solution; m (g) is the mass of the adsorbent.

2.3.3 MB adsorption isotherm

The adsorption isotherms were carried out at different concentrations, in optimal conditions established in the kinetic study ($m = 22.5 g .L^{-1}$, pH = 6.9-7.1, T = 25 °C, stirring velocity = 200 rpm, contact time 30 minutes). The suspensions were then analyzed as described previously.

3. Results and Discussion

3.1 Characterization of the material

3.1.1 Chemical composition of silica

The chemical composition of the natural silica was carried out by X- ray fluorescence.

The obtained results are presented in (Table 1).

Table 1: Chemical composition of natural silica

Component	SiO ₂	Al ₂ O ₃	MgO	P ₂ O ₅	Fe ₂ O ₃	CaO	MnO
% (mass)	93.32	1.35	1.34	0.33	0.56	0.26	0.01

3.1.2 XRD spectrum of silica

The XRD spectrum of our sample (Fig.2) shows a major peak at 2 θ (26.9) which is characteristic of SiO₂. Some other peaks at 2 θ (36.8, 39.9, 50.07, 55.71, 60.09, and 68.93) can be attributed to the quartz and other phases containing silicon oxide.

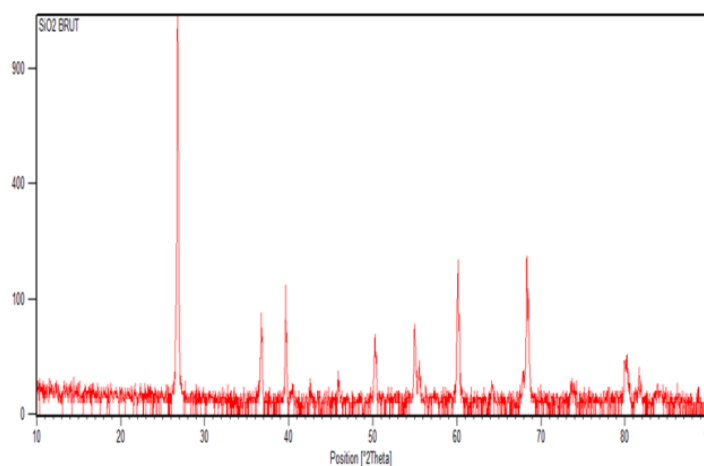


Fig 2: Diagram of X-ray diffraction of natural silica.

3.1.3 IR spectrum of the silica

The FT-IR spectrum of the natural silica (fig.3) showed a peaks at 571 and 535 cm⁻¹ represent the bending vibrations of Si-O-Si.

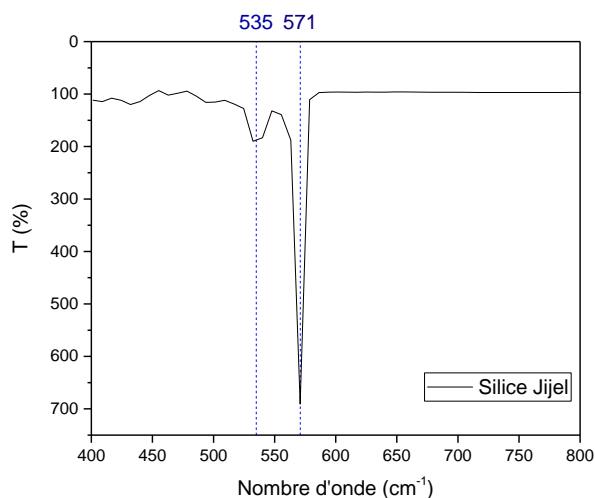


Fig 3: IR spectrum of natural silica

3.1.4 SEM analysis

The result of SEM analysis of natural silica is shown in Fig. 4. SEM images, at 10, 50 and 500 μm dimensions show that the natural silica has random particle shapes. Furthermore, image at 10 μm shows that the natural silica has a porous surface.

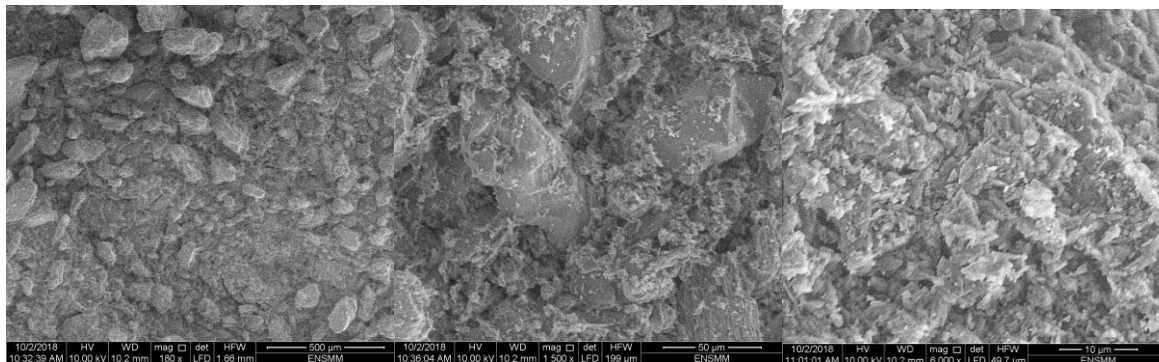


Fig 4: SEM images of natural silica.

3.2 Effect of the mass of adsorbent

The results show that the % of discoloration of the MB solution increases as the mass of silica increases. Beyond a mass of material of 0,45g, the rate tends to be stabilized with appearance of a saturation stage (Fig 5).

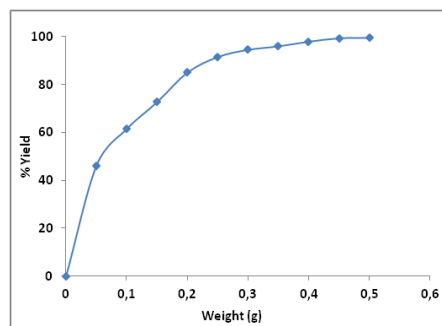


Fig 5: Variation of % of discoloration according to the mass of silica $C_0 = 80\text{ppm}$, $\text{pH} = 6.9$, $T=25^\circ\text{C}$.

3.3 Kinetics study

3.1 Effect of the initial concentration

Examination of Fig 6 shows that the equilibrium is generally reached after 30 minutes of contact for the different initial concentrations of MB. It can be seen that an adsorption yield of 96% is reached in just 15 minutes and it corresponds to a sufficient removal of dye. This phase corresponds to a transfer of the adsorbate from the liquid phase to the surface of the material. This phenomenon observed during the first minutes of the reaction, can be interpreted by the fact that at the beginning of adsorption, the number of

active sites available at the surface of the adsorbent material, is much greater than that of the remaining sites after a certain time. After 15 minutes the adsorption becomes slower leading to a slight improvement of elimination of MB (2%). This zone corresponds to the saturation of the solid surface.

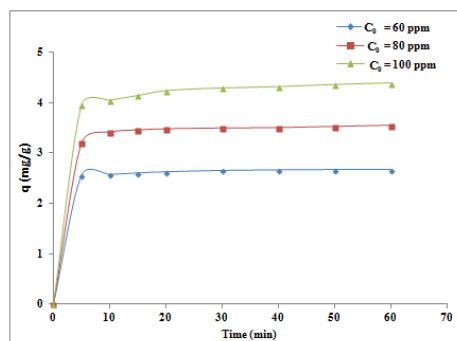


Fig 6: Effect of the initial concentration on the adsorption of MB on natural silica (T=25°C, pH = 6.9, Va=200 rpm).

3.2 Effect of stirring velocity

In order to study the effect of mixing on the retention process, three agitation velocities were considered: 100, 200, 300 rpm. Figure 6 shows that the mixing speed acts favorably on the MB retention early in the process and it starts to decrease as time passes, in fact, saturation is reached. This can best be seen on the second part of the curves.

The phenomenon observed in Fig. 7 could be explained by the fact that the increase in stirring speed improves the transfer of the methylene blue ions to the solid support.

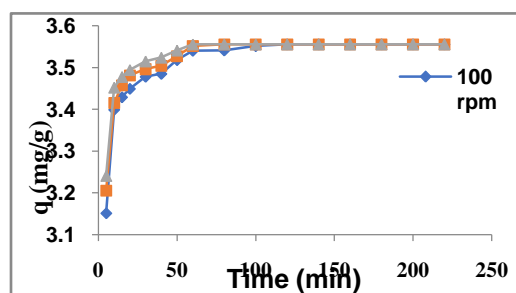


Fig 7: Influence of stirring velocity of the adsorption of the MB (C₀ = 80 ppm, pH = 6.9, T=25°C).

3.4 Effect of temperature

To study the influence of temperature on the retention of MB, three different temperatures were selected 25, 35, and 45°C. From Figure 8 one can notice that the temperature has a similar effect on the retention of the MB as the mixing velocity. An increase in temperature results in a relatively considerable improvement of the adsorption capacity, which becomes less efficient after 20 min of contact.

Therefore, an explanation similar to the one given for the effect of mixing velocity can most probably be given for the effect of this parameter, in a sense that an increase in temperature supply the ionic specie with an energy to surpass the repulsive forces up to a certain extent and then becomes inefficient (state of saturation)³¹.

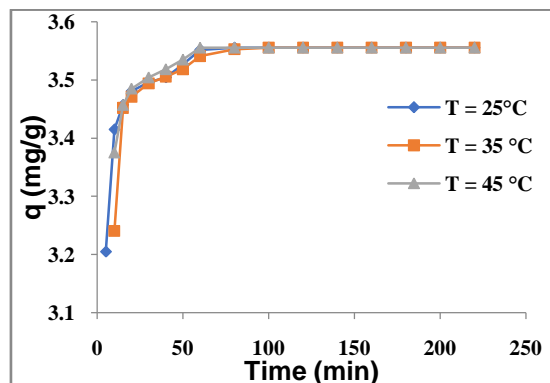
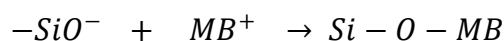
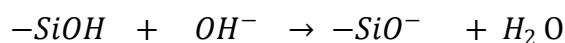
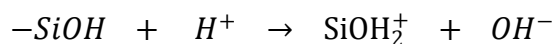


Fig 8: Effect of temperature on the adsorption of the MB on natural silica ($m=22.5g/l$, $C_0 = 80ppm$, $pH = 6.9$, $V_a = 200 rpm$).

3.5 Effect of the pH

Figure 9 shows the effect of the pH on the removal of the MB by the natural silica. It can be seen that when the pH solution increases from 2 to 12, the rate of adsorption rises from 76% up to 98%. It is thus clear that an increase in the pH is favorable to the formation of the $-SiO^-$ grouping therefore to an increase of negative electric charges on the surface of silica which leads to an electrostatic attraction of the MB (R^+ , Cl^-) due to its positive charge in solution.

This mechanism is represented by the following reactions



A similar theory has been proposed by several works for the adsorption of metals on various adsorbents³²⁻³⁴.

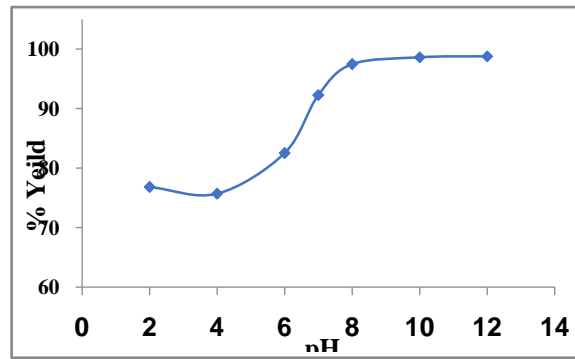


Figure 9: Effect of pH on the adsorption of the MB (m=22.5g/l, T=25°C, Va = 200 rpm, C₀ = 80ppm).

4. Kinetic modeling

The studies of adsorption equilibrium are important in determining the effectiveness of adsorption; however, it is also necessary to identify the types of adsorption mechanism in a given system. In this study we used three different models to predict the adsorption kinetic of MB on natural silica (pseudo-first order, pseudo-second order, and intra-particle diffusion models).

- **Pseudo-first-order model:** it is one of the most widely used sorption rate equation to simulate the adsorption kinetic^{35,36}. The model equation is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Where t: contact time; k_1 : constant of adsorption speed of the kinetic, q_t and q_e : adsorption capacities, respectively, at the moment t and at equilibrium. The linear pseudo-first-order plots for the adsorption of MB onto natural silica are shown in Fig 9(a). The related parameters are listed in table 3. It can be seen that the R^2 values are low; moreover, the difference between the values of the experimental and the calculated q_e is very important. This indicates that the adsorption of MB on natural silica does not fit a pseudo-first-order kinetic model.

- **Pseudo-second-order model:** based on equilibrium adsorption, the pseudo-second-order kinetic equation³⁷ is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

Where t: contact time; k_2 : constant of adsorption speed of the kinetics, q_t and q_e : adsorption capacities, respectively, at the moment t and at equilibrium. As shown in Fig 9(b) and Table 3, there was an excellent agreement between the experimental and the calculated q_e values. The obtained R^2 values indicate that the adsorption of MB on natural silica follows the pseudo-second-order model.

- Intra-particle diffusion model:** The pseudo-first-order and pseudo-second-order kinetic models could not identify the diffusion mechanism. Therefore, the kinetic results were then analyzed by using the intra-particle diffusion model. In the model developed by Weber and Morris³⁸⁾, the initial rate of intra-particle diffusion is calculated by the linearization of equation (5):

$$q_t = k_W t^{1/2} + C \quad (5)$$

Where C is the intercept and k_W the intra-particle diffusion rate constant ($\text{mg/g min}^{1/2}$). According to this model, the plot of uptake, q_t , versus the square root of time ($t^{1/2}$) should be linear if intraparticle diffusion is involved in the adsorption process and if these lines pass through the origin then intra-particle diffusion is the rate-controlling step³⁹⁾. As shown in Fig 9 (c), the straight lines did not pass through the origin, this is an indicative of some degree of boundary layer control and there also show, that the intra-particle diffusion is not the only rate-limiting step, other kinetic models may also control the rate of adsorption, all of which may be operating simultaneously^{40,41)}. The values of the intercept (C in Table 3) also give an idea about the boundary layer thickness: the larger the intercept, the greater is the boundary layer effect. It was observed from the table (3) that there is an increase in the value of C, this indicates the abundance of solute adsorbed on boundary layer.

Table 2: Kinetic parameters of the different used models

Modèle		Paramètres	
PFO		$q_{e,exp}$	3.555
		$q_{e,cal}$	0.349
		k_1	0.063
		R^2	0.858
PSO		$q_{e,cal}$	3.571
		k_2	2.187
		R^2	1,000
Intra particule diffusion	Step I	k_W	0.050
		C	3.257
		R^2	0.987
	Step II	k_W	0.024
		C	3.354
		R^2	0.937
	Step III	k_W	0
		C	3.555
		R^2	-0.600

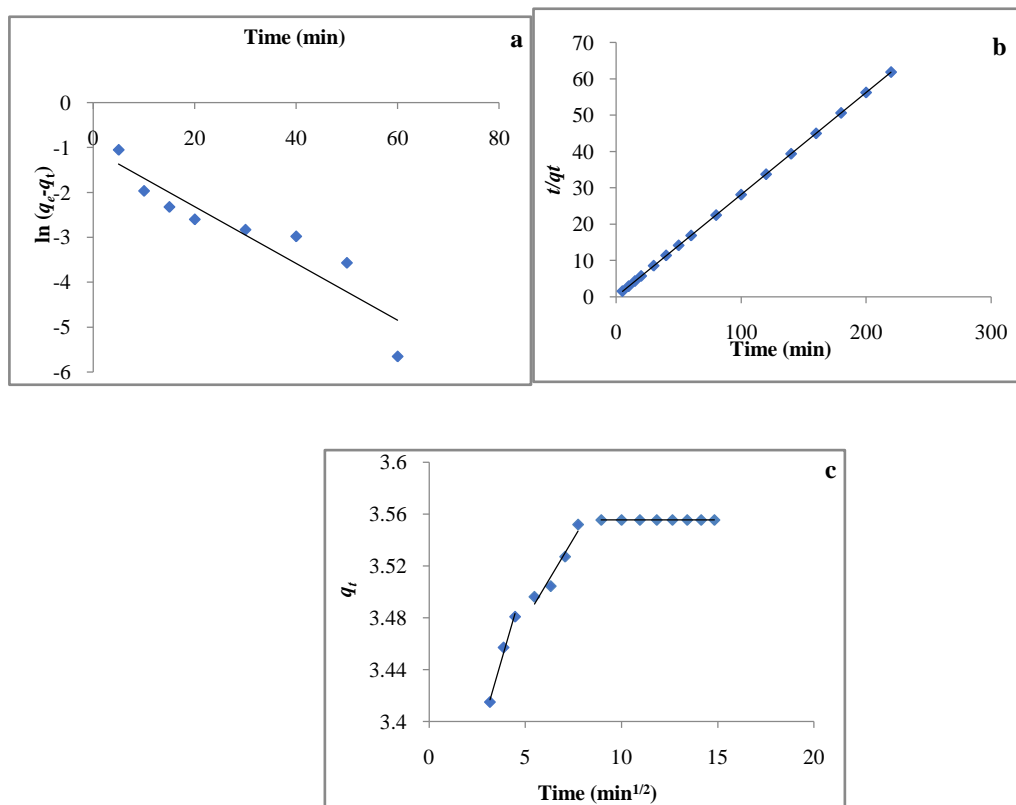


Fig 10: Linear regression of various kinetic models (a) PFO, (b) PSO, (c) intra particle diffusion.

5. Adsorption isotherms

According to Gilles classification [42], experimental results which show a growth of adsorption with an increase of the adsorbate concentration (Fig. 10) indicate that the isotherme is of type S.

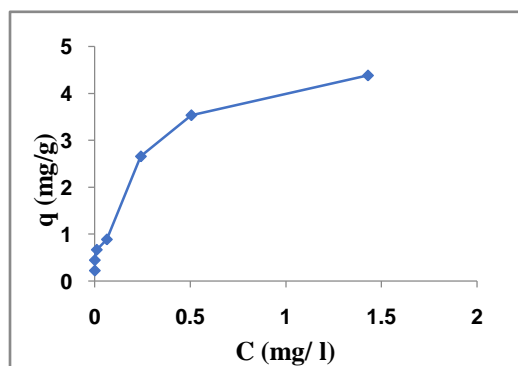


Fig 11: Isotherm of adsorption of MB on natural silica $V = 20\text{ml}$; $V_a = 200$ rpm; $T = 25^\circ\text{C}$; $\text{pH} = 6.9$.

The examination of the isotherms of Langmuir⁴³⁾ and Freundlich⁴⁴⁾ would allow calculation of the maximum quantity adsorbed by the solid. The modeling equations of Langmuir (Eq. 7) and Freundlich (Eq. 8) isotherms, in adsorption their linearized forms, are as follows:

Table 3: Adsorption parameters of MB on natural silica

Model					
LANGMUIR			FREUNDLICH		
(mg/g)	b (mg/g)		n	(mg/g)	
4.926	5.342	0.981	2.342	4.108	0.93

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{b q_m} \quad (7)$$

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (8)$$

Where q_e : adsorption capacity of the solute per gram of adsorbent at equilibrium (mg g^{-1}); q_m : Langmuir maximum adsorption capacity (mg g^{-1}); C_e : concentration of the solute at equilibrium (mg L^{-1}); b : constant of Langmuir connected to the energy of adsorption (L mg^{-1}); k_F and n : empirical constants of Freundlich representing, respectively, the capacity and the intensity of adsorption.

The study of Langmuir and Freundlich adsorption isotherms are represented in Fig. 12 and Table 5. From these results, according to the values of R^2 (Table 5), it is clear that the Langmuir model is the most suitable.

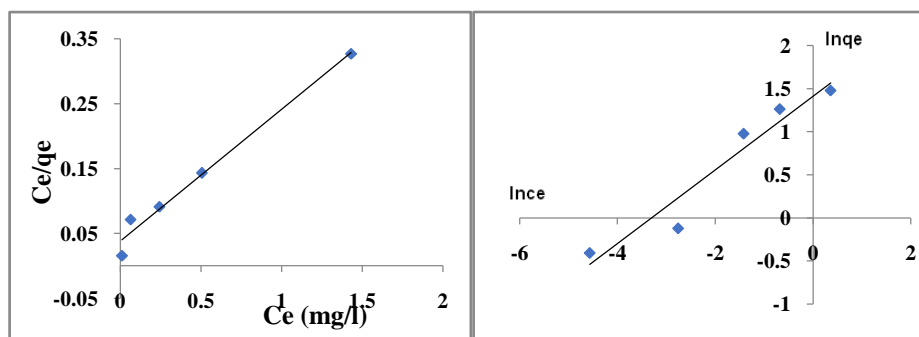


Fig 12: Adsorption isotherm of MB on natural silica according to (a) Langmuir model, (b) Freundlich model ($V = 20 \text{ ml}$, $V_a = 200 \text{ rpm}$, $m = 0.45\text{g}$, $T = 25^\circ\text{C}$, $\text{pH} = 6.9$).

Table 4: Comparison of the adsorption of the MB by natural silica and by other adsorbants.

Materials	pH	Adsorption %	Reference
Silica Gel	10	95.2	-45
Fly ash	6	93.73	-46
Raw sugarcane	7	100	-47
bagasse modified orange II	2	100	-47

Carbon nano tubes (CNTs)	4-Feb	90	-48
commercial charcoal CECA40	6	93	-49
Natural silica	6.8-7.1	98	This study

6. Conclusion

The results obtained in this work have shown that:

- Increase of the mass of the adsorbent, the stirring speed, the temperature, and the initial concentration had a positive influence on the capacity and kinetics of retention of the MB on natural silica.
- According to the high values of the correlation coefficients (R^2), the adsorption kinetic is best described by the pseudo-second-order model.
- The isotherm of adsorption of MB on natural silica was better described by the Langmuir model.
- The optimal conditions for the adsorption of the MB by natural silica were found to be $m = 22.5$ g/l, $V_a = 200$ rpm, $T = 25$ °C, and $pH = 8$. The ultimate adsorption capacity was equal to $q = 3.5713$ mg/g.

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